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Vibrational Spectroscopic Identification of Protonation and Oxidation States of DMcT

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Abstract: In this contribution we report some initial results of our solid phase vibrational spectroscopic study of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) and derivatives representing its protonation and oxidation states. We have succeeded in assigning observed bands to modes which are diagnostically useful for studies concerning the electrochemical character of DMcT when used with polyaniline (PAn) as a composite cathode material in a secondary lithium ion cell. We also discuss the implications of the current study for our further investigations of the DMcT/PAn cathode.

Introduction

Previously, we have reported the use of a composite material consisting of an organosulfur compound (2,5-dimercapto-1,3,4-thiadiazole, or "DMcT") in concert with a molecular wire (polyaniline, or "PAn") as the cathode of a Li ion secondary battery.[1-3]

Our recent results indicate that the redox processes of DMcT are accelerated in the presence of a weak base.[4-7] We have attributed this acceleration to a moderation of the local proton activity by the weak base. Elucidation of this effect represents a conceptual breakthrough for us and has allowed us to focus our efforts to careful consideration of the proton transfer processes which occur in the cathode material. Toward this end, we have become interested in using infrared (IR) spectroscopy to investigate the oxidation and protonation states of DMcT and PAn during the charging and discharging processes of the cell. While the vibrational assignments for PAn have been studied in great detail,[8] a survey of structural assignments based on the vibrational band data in reports available for DMcT reveals many inconsistencies.[9-13] Therefore, we have concentrated on providing conclusive assignments of the vibrational modes of DMcT in its various protonation and oxidation states. However, we have limited our assignments to those bands which are useful as diagnostic indicators of the various states of DMcT. Furthermore, due to the complexity of the spectra, we have initially investigated the compounds in the solid state only.

Experimental

Spectroscopy was performed using a Bio-Rad 60 FTS/896 FT-IR instrument equipped with a Raman attachment and a mercury-cadmium-telluride (MCT) detector (IR measurements) or a Ge detector (Raman measurements). Raman spectra represent 1024 co-added scans taken at 4 cm^{-1} resolution. IR spectra represent 512 co-added scans taken at 2 cm^{-1} resolution.

Details of the chemical synthesis of the protonation and oxidation forms of DMcT will be reported in a future communication.

Results

Tautomeric Structure of DMcT and derivatives

The results of crystallographic studies indicate that (in the solid state) DMcT exists predominantly in the thiol/thione form[14] (Scheme 1) and di-DMcT exists primarily in the thione/thione form[15] (Scheme 1). These structures are reflected in the vibrational spectra reported below. In the absence of other reports on the structure of LiDMcT, we have assigned its predominant tautomer form as the thione form using the vibrational bands signature of the thioamide group (*vide infra*).

Vibrational Spectra

IR and Raman spectra were obtained for DMcT and three derivatives (shown in Scheme 1). These spectra are presented in Figure 1. The objective of this study was to allow for the unambiguous determination of the oxidation state and the state of protonation of DMcT in the context of its use in battery systems. Thus, the assignments of these spectra are not complete. Rather, we have concentrated on identifying those modes that are diagnostic of the redox and acid/base chemistry of these compounds.

Table 1 details our assignment of the observed bands to the various modes in the molecules. In particular, we have assigned the C=N stretch (split when the ring includes two C=N bonds) to bands at ca. 1400 to 1450 cm^{-1} (based on the skeletal

vibrations for pyrrole and furan[16,17]), the N-N stretch to a band near ca. 1025 cm^{-1},and C-S-C asymmetric and symmetric stretches to bands at ca. 720 and 660 cm^{-1}, respectively.[18,19] Also, a strong band near 1280 cm^{-1} is assigned to an A1 mode that is predominantly due to an out of phase combination of the N-N and symmetric C-S-C stretches. Modes of this type are frequently observed in the IR spectra of diene-like five membered rings, with pyrrole and furan being the parent examples,[16] although this band has not been assigned for the DMcT family of compounds previously to this work.

The predominant tautomer forms of the compounds is established to be the thione forms (boxed in Scheme 1) by the presence of several bands in the spectra which are characteristic of this tautomer.[20] These bands include the N-H bend near 1505 cm^{-1} in the IR, the single C=N stretch, and the band near 1280 cm^{-1} which can be assigned to the thioamide II mode.[12d,21] The latter mode is generally assumed to be a combination of C-N and C=S stretching and N-H bending for acyclic thioamides here we assign this mode predominantly C-N stretch character. Also for the thioamide group, the bands from ca. 3200 to 2600 cm-1 have been assigned by Suzuki[21] to overtones of the thioamide group, stretching of the N-H bond, and Fermi resonances between those two modes. We have not assigned these peaks because they are not diagnostically useful. Note that the C=N stretching frequencies in both this compound (1405 cm^{-1}) and the dianion of DMcT (1393, 1372 cm^{-1}) are quite low due to the electron donating character of the thiolate group.

A major outcome of this study is that the spectral characteristics of these compounds provide a relatively comprehensive basis from which to unambiguously determine both the oxidation state and the degree of protonation of DMcT and its derivatives. The fact that vibrational spectroscopy can be employed for this purpose is particularly attractive because of its ease of use as an *in situ* tool in electrochemical studies. Thus, the present work serves as a prelude to a thorough *in situ* vibrational spectroscopic study of the redox and acid/base behavior of the DMcT/poly(aniline) lithium secondary cathode system.

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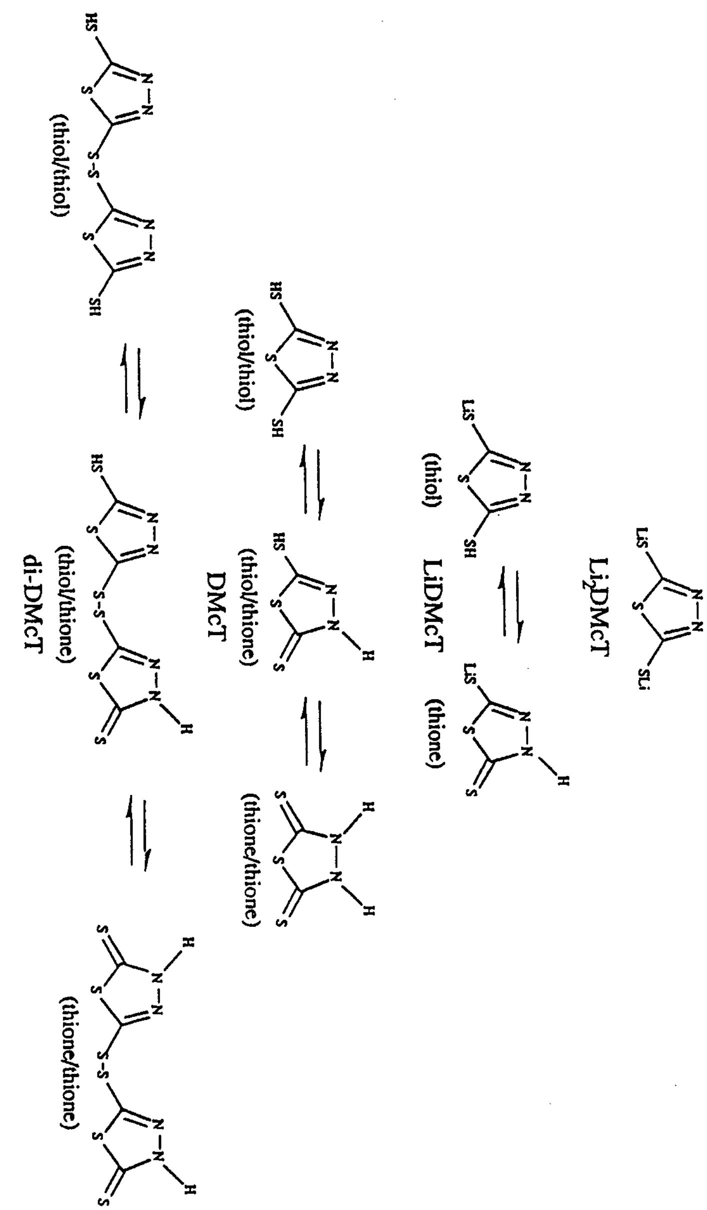
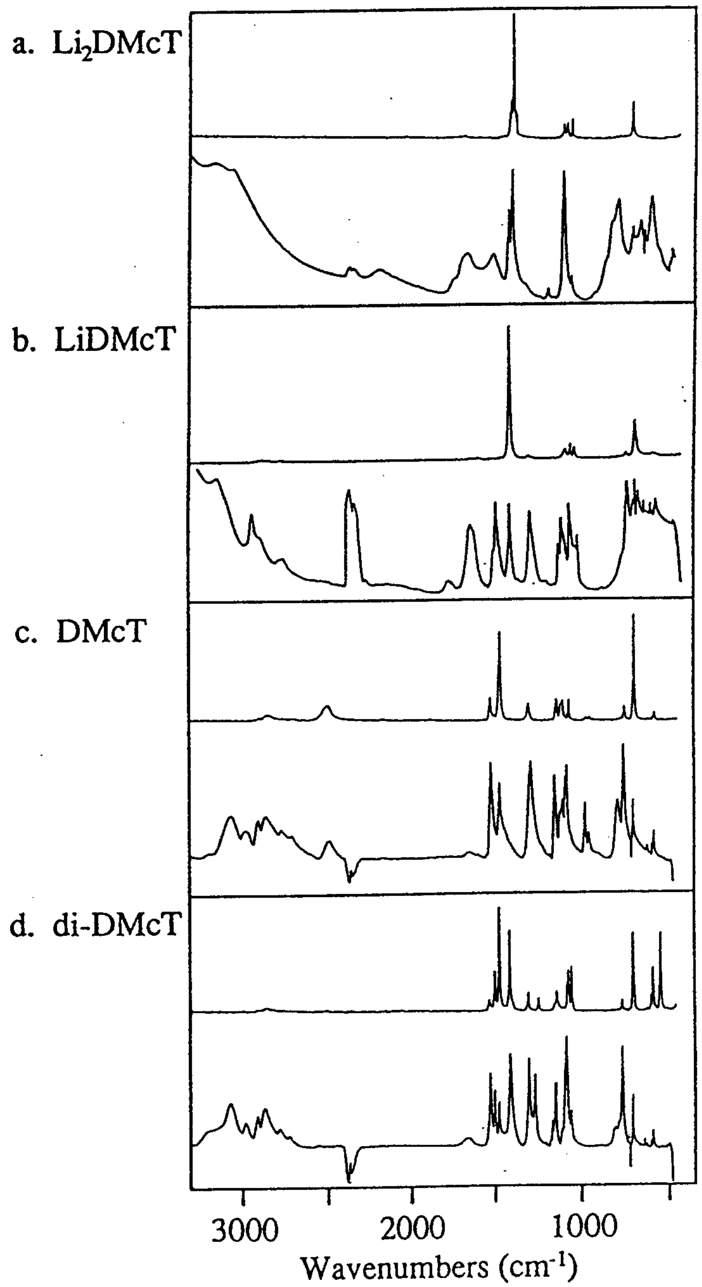
Figure caption: Vibrational spectra of the compounds studied. (a) shows the Raman (top) and IR (bottom) spectra of Li_2DMcT. (b) shows the Raman (top) and IR (bottom) spectra of LiDMcT. (c) shows the Raman (top) and IR (bottom) spectra of DMcT. (d) shows the Raman (top) and IR (bottom) spectra of di-DMcT.

Table 1: Vibrational Band Assignments for DMcT and Derivatives

Li_2DMcT Raman	Li_2DMcT IR	LiDMcT Raman	LiDMcT IR	DMcT Raman	DMcT IR	di-DMcT Raman	di-DMcT IR	Primary Contributing Mode or Modes
		ca. 3200-2700		ca. 3200-2700		ca. 3250-2700		ν(N-H), overtones, and Fermi resonances
				2483	2480	2486vw	2491vw	ν(S-H)
		1501vw	1503	1508	1506	1506	1501	δ_{ip}(C-N-H)
		1402	1405	1448	1452	1473	1474	ν(C=N)
						1446	1449	
	1393							ν_{as}(C=N)
1375	1372							ν_s(C=N)
		1307	1290	1279	1265	1274	1271	thioamide II mode
1024	1021	1026	1030	1038		1107		ν(N-N)
1072	1068		1388					A1 ring mode
				941	938			ν(C=S)
					750			τ(N-H)
	751	722	720	712	715	717	718	ν_{as}(C-S-C endocyclic)
671	669	668		656	659	650	655	ν_s(C-S-C endocyclic)
						532		ν(S-S)

ν = stretch, = deformation, = torsion, ip = in-plane, as = asymmetric, s = symmetric





a. Li_2DMcT
b. LiDMcT
c. DMcT
d. di-DMcT
3000
2000
1000
Wavenumbers (cm^{-1})